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LUMINESCENT DECAY OF VARIOUSLY PRETREATED KCl: Tl PHOSPHORS

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(*Received July 9, 1966 · Resubmitted November 12, 1966*)

ABSTRACT. Room temperature measurements of the phosphorescence decay are made in untreated and pretreated KCl : Tl phosphors. Pretreated phosphors consist of specimens prepared with different heat treatments followed by deformation or in the undeformed state. The results obtained are analysed in terms of the concept that in the room temperature region the electron traps are due to negative ion vacancies. It is suggested that various types of negative ion vacancies exist depending on their location in the normal and distorted regions of the lattice. In the latter types the charged dislocations are presumed to play an important role.

INTRODUCTION

There have been a number of attempts at offering interpretations which would adequately explain the room temperature phosphorescence decay in KCl : Tl. Seitz (1938) interpreted it on the basis of the internal metastable states of the Tl^+ ions occupying substitutional positions in the host lattice. This was supported by Johnson and Williams (1953). Later work however showed that the electron traps are independent of the impurity ions and are formed by other crystalline imperfections in the host lattice (Ewles and Joshi 1960).

In all the earlier decay studies of the phosphor no particular attention has been given to the previous history of the sample. Therefore it is considered worthwhile to study the decay characteristics of the phosphor intensively under the influence of as many different factors as possible. The present work, concerned primarily with obtaining necessary data, specifically deals with the effects of thermal treatment, of deformation and of thermal treatment followed by deformation, on the decay of the phosphor at room temperature. Interpretations of the results obtained are offered on the basis of the concept advanced earlier that electron traps are due to single negative ion vacancies in different environments (Joshi 1964). It has been suggested before that the electrostatic interaction between dislocations, presumed to be charged, and negative ion vacancies may be important (Joshi and Menon 1965). This analysis is extended to the present work. The various components of the decay are considered to be due to differences in the degree of electrical interaction.

EXPERIMENTAL PROCEDURE

All the KCl : Tl specimens used in the experiment were prepared from postassium chloride of 'analar' grade by crystallisation from aqueous solution. The results presented are for KCl : Tl phosphors containing 0.0015 and 0.003 mol. of Tl. Measurements were made on the following samples : (i) as—obtained from solution (ii) annealed and slowly or rapidly cooled (iii) as—obtained and deformed and (iv) heat-treated and deformed. Annealing of the samples was carriedo ut in a 'muffle' furnace, held at 300°C for 100 hours. With a suitable temperature control, the sample could be cooled very slowly at a rate of 1.5°C/hr. In the case of rapid cooling, the sample was withdrawn from the furnace after anneal at 300°C for 100 hours and then air-cooled. All annealings were carried out in evacuated and sealed Pyrex tubes. The sample, either *as*-obtained or heat-treated, was compressed to tablet in a chromium plated stainless steel press under a pressure of about 2000 kg/cm^2.

An account of the experimental technique has been presented previously (Joshi 1964). The sample was excited with ultraviolet light from a high pressure mercury discharge lamp, the excitation time in each case being 1.5 min. Phosphorescence decay measurements, following irradiation, were made using RCA

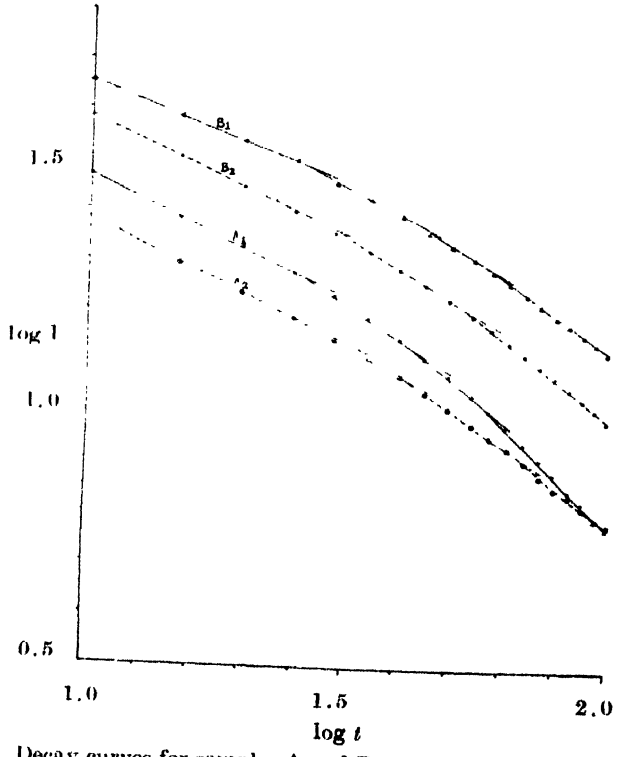

Fig. 1. Decay curves for samples A and B
Curves : A_1 and B_1 for Tl conc. 0.0015 mlf.
„ : A_2 and B_2 „ „ „ 0.003 ml.f.

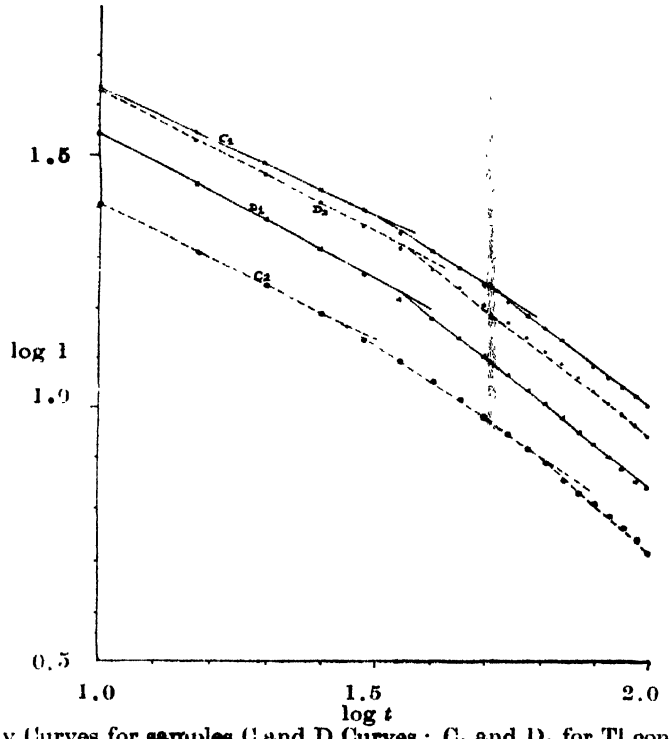

Fig. 2. Decay Curves for samples C and D Curves : C_1 and D_1 for Tl conc. 0.0015 m.f.
: C_2 and D_2 „ „ „ 0.003 m.f.

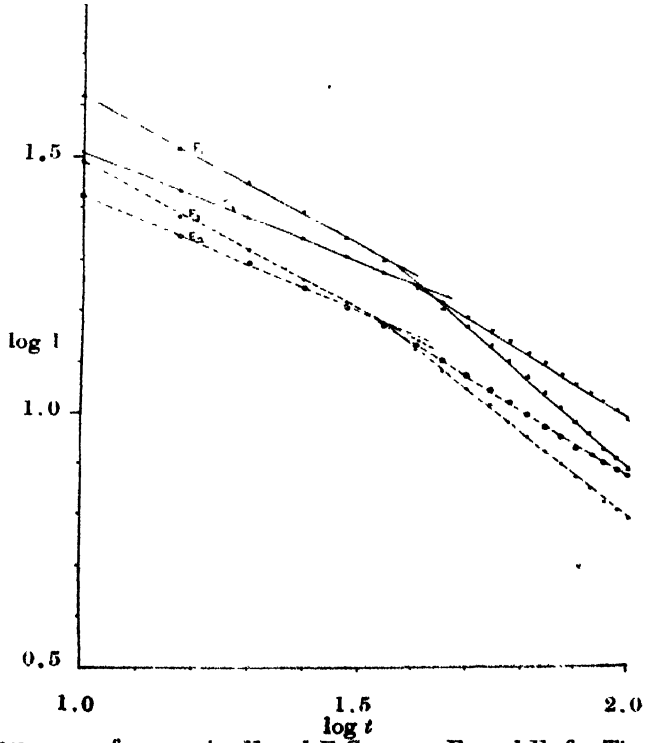

Fig. 3. Decay curves for samples E and F Curves : E_1 and F_1 for Tl conc. 0.0015 m.f.
: E_2 and F_2 „ „ „ 0.003 m.f.

galvanometer. All the measurements were made at room temperature in total darkness.

EXPERIMENTAL RESULTS

Figures 1 to 3 indicate the results of the experiments performed with as-obtained and variously pre-treated KCl : Tl specimens. In all the figures log-log 931A photomultiplier the output of which, after amplification, was fed to a mirror plots of intensity (I) against time (t) show that the results can be fitted very well to the power law decay $I = I_0 t^{-n}$. Measurements were made on two KCl : Tl phosphors differing in their Tl content. Apparently there is no difference in the decay behaviour of the two phosphors. The decay curves for as-obtained or heat-treated samples show distinct curvatures. These curves can be fitted to suggest 3 to 4 independent first order processes. The noteworthy feature of the data presented in the figures is that in general, the number of decay components reduces to two if as-obtained or heat-treated specimen is deformed by stressing. A list of the samples used in the experiments, then ature of the physical treatment received by each sample and the values of the decay constants (n) for ultraviolet emission are indicated in Table I. Similar results were obtained for visible emission.

TABLE I

Sample : A – As -obtained from solution
B – Sample A annealed at 300°C for 100 hrs., slowly cooled.
C Sample A annealed at 300°C for 100 hrs., rapidly cooled.
D Sample A compressed into tablet
E Sample B compressed into tablet
F Sample C compressed into tablet

Decay constant (n) values for different stages (U.V. emission)

Sample	Tl Content 0.0015 mol.	n	Tl Content 0.003 mol.	n
A	A_1	0.47, 0.65, 0.82, 1.0	A_2	0.48, 0.54, 0.68, 0.82
B	B_1	0.39, 0.52, 0.61, 0.73	B_2	0.46, 0.61, 0.82
C	C_1	0.51, 0.65, 0.84	C_2	0.54, 0.72, 0.96
D	D_1	0.58, 0.85	D_2	0.57, 0.85
E	E_1	0.43, 0.65	E_2	0.46, 0.66
F	F_1	0.58, 0.92	F_2	0.58, 0.85

DISCUSSION

It is seen from the results that the decay curve for as-obtained or heat-treated specimens can be resolved into more than two concurrent first order processes. In general, the number of decay stages reduces to two if the as-obtained or heat-treated specimen is compressed by stressing. Similar results have been reported earlier by Morlin (1957). In a log-log plot he observed two linear stages for decay in the case of NaCl : Tl phosphors either in the form of discs prepared from powder or in the form of single crystals deformed by stressing. On the other hand, he found the plot for an undeformed single crystal phosphor to be a non-linear curve in the same diagram. These results can be understood if one attempts an explanation in terms of the electron traps due to single negative ion vacancies in different surroundings. It is suggested that the fastest component of the decay is due to phosphorescence Centres each of which consists of a combination of a negative ion vacancy (trap) with an adjacent stubstitutional Tl^{+} ion (emission centre). Such phosphorescence centre form one category. The remaining components of the decay are due to phosphorescence centres each of which is composed of a similar combination as stated above but in the vicinity of an edge dislocation presumed to be negatively charged. This phosphorescence centres fall in second category. In the second category the phosphorescence centres are further differentiated on the basis of the distance of separation between the dislocation and the negative ion vacancy—Tl^{+} ion complex. Variation in the distance of separation would lead to the difference in the degree of electrical interaction between them and correspondingly the lifetimes of the traps belonging to the second category would differ. It is suggested that the charge on the dislocation is small. That is a dislocation will not measurably influence the decay process if the distance of separation between it and the vacancy $-Tl^{+}$ ion complex is large say, fifty lattice spacings or more.

During plastic deformation a small stress can give rise to dislocation motion in the microcrystals of the phosphor. If during motion a dislocation comes in the close vicinity of a Tl^{+} ion it will be pinned or immobilised by its interaction with the impurity ion. It is believed that as a result of plastic deformation the dislocation is pinned at the Tl^{+} ion in majority of the phosphorescence centres of the second category. Hence the phosphorescence centres obtained after deformation would involve either a combination of a Tl^{+}ion and adjacent negative ion vacancy or a similar combination closely associated with a charged dislocation. The rate of release of electron in any of the latter species of phosphorescence centres will be affected by dislocation more or less to the same extent. It is suggested that the two components of the decay observed after plastic deformation in all the samples are due to the above two types of the phosphorescence centres.

ACKNOWLEDGMENTS

We wish to express our thanks to Dr. N. S. Pandya for encouragement. One of us (A.K.M.) gratefully acknowledges the award of a Fellowship from the Council of Scientific and Industrial Research, New Delhi.

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